

DESCRIPTION OF THE PLATES.

PLATE VIII.

- Fig. 1. *Felis leo* (max.).
 2. — *tigris* (max.).
 3. — *jubata* (mean).
 4. *Ursus ferox* (mean).
 5. — *arctos* (mean).
 6. — *maritimus* (mean).
 7. *Hyena crocuta* (mean).
 8. — *brunnea* (mean).
 9. — *striata* (mean).

PLATE IX.

- Fig. 10. *Canis lupus*.
 11. — *aureus*.
 12. — *vulpes*.
 13. — *bengalensis* (fossilis).
 14. — — (hodie).
 15. — *zerda*.
 16. *Sus scrofa* (ferus).
 17. — *domesticus*.
 18. *Equus caballus*.

XI. "Note on the Spectra of Erbium and some other Earths." By
 WILLIAM HUGGINS, LL.D., F.R.S. Received May 26, 1870.

Bahr and Bunsen have shown* that erbium, rendered incandescent in a Bunsen's gas-flame, gives a spectrum of bright lines in addition to a brilliant continuous spectrum. As they were unable to discover the bright lines in the flame beyond the limits of the solid erbium, they suggest that the light which is dispersed by the prism into bright lines is emitted by the solid erbium, which substance therefore appears to stand alone, as a remarkable exception, among solid bodies. Bahr and Bunsen found the spectrum of bright lines to coincide very nearly with the absorption spectrum of some compounds of erbium.

A few weeks since, when in Ireland, I made the observation that the spectrum of the ordinary lime-light contains bright lines†. Dr. Emerson Reynolds, Director of the Laboratory of the Royal Dublin Society, kindly undertook to make experiments to ascertain from the position of the lines if they were due to the cylinder of lime, or to impurities contained in it.

Upon my return to town I made the following experiments; shortly after commencing them I received from Dr. Reynolds the account of his experiments, which, with his permission, I have added to this note.

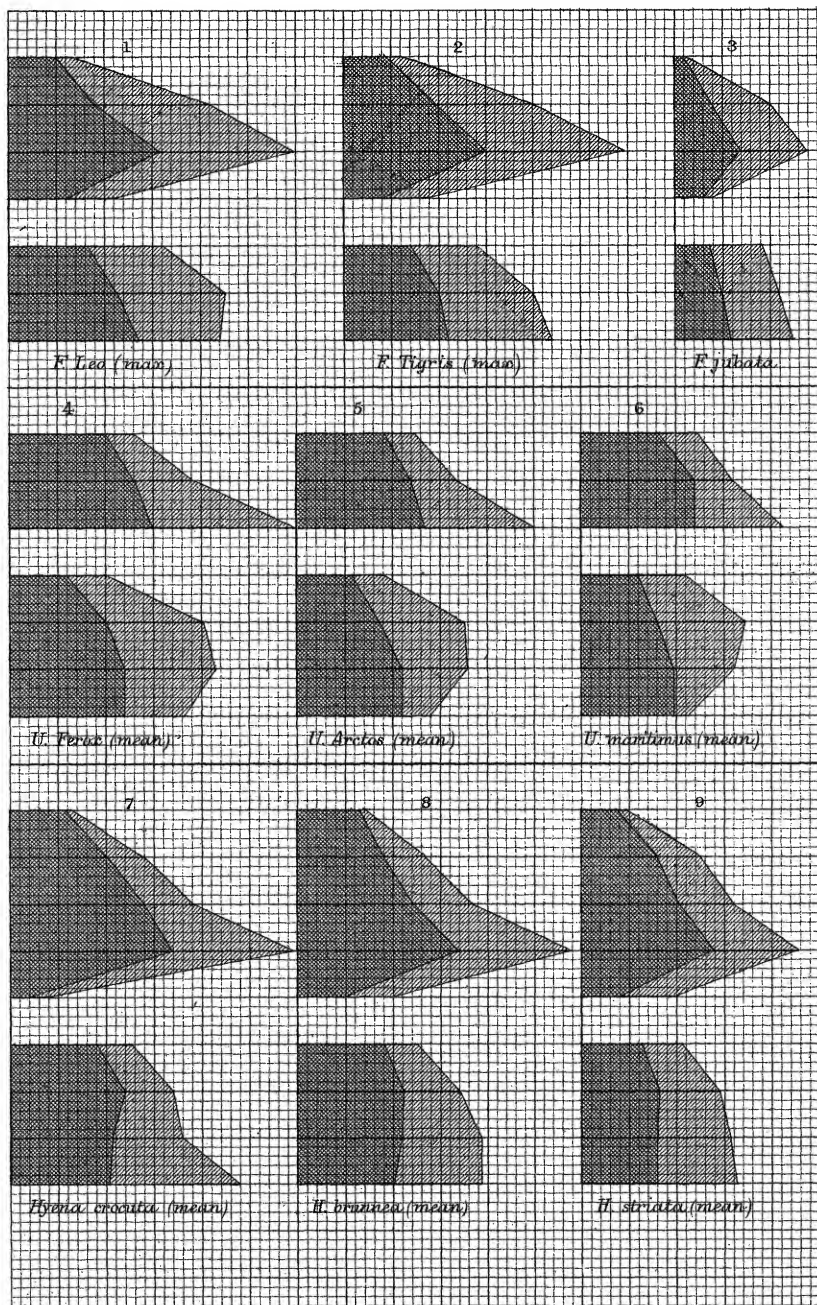
Erbium.—A few months since I received, through the kindness of Dr. Roscoe, F.R.S., a few grains of nitrate of erbium, which he had procured from a trustworthy source. I followed Bunsen's method of placing it with syrupy phosphoric acid upon a platinum wire. The erbium, obtained by this method in a finely divided state, was then submitted to the heat of the oxyhydrogen blowpipe.

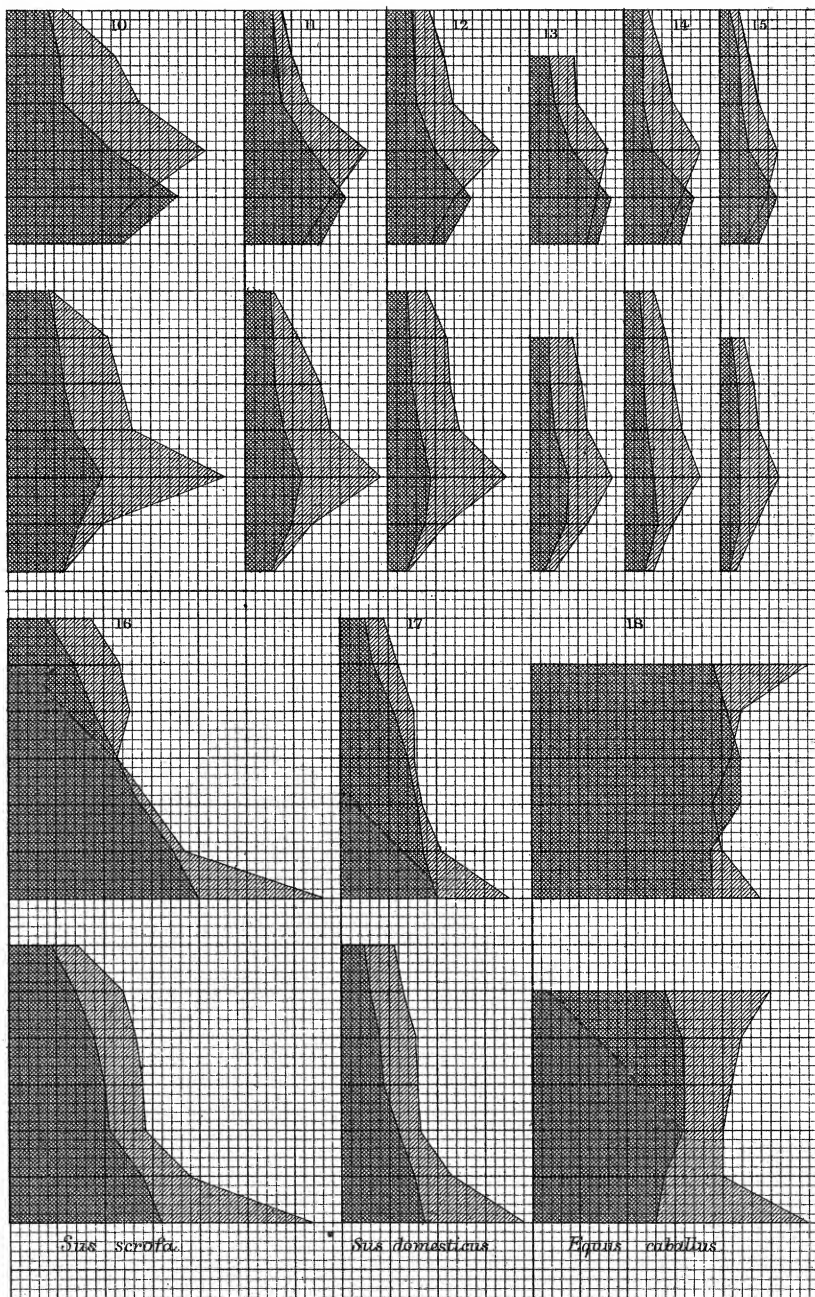
In all the experiments described in this paper hydrogen alone was first turned on, and the effect of the heat of the flame on the substance under examination observed with the spectroscope. Oxygen was then admitted slowly, and the effect of the increased heat carefully noted.

With the flame of hydrogen alone, the lines represented in the map

* Liebig's Annalen, Bd. lxi. (1866) S. 1.

† Dr. W. Allen Miller informs me that in 1845 he noticed a bright line in the spectrum of the diffused light of the oxyhydrogen jet reflected from a sheet of paper.





which accompanies Bahr and Bunsen's paper were seen, but the lines were more distinct when a small proportion of oxygen was admitted. With the full proportion of oxygen, the light from the glowing erbia was more intense, but the lines were not so well seen. Even with the intense heat of the oxyhydrogen flame I was unable to trace the lines beyond the limits of the solid erbia, though the line of sodium could be seen for some distance from the erbia. I found, however, that the lines appeared more distinct, in consequence, probably, of their being brighter relatively to the parts of the continuous spectrum where they occur, when the slit was directed from the side upon the gas immediately in front of the glowing part of the erbia.

The spectrum of bright lines obtained by means of the oxyhydrogen flame agreed more completely with the absorption spectrum represented by Bahr and Bunsen (No. 2 in their diagram) than the spectrum of bright lines figured by those observers (No. 3). The most important differences occurred in the band in the red, which showed two points of greatest brightness, thus forming a double line with a little outstanding light, and the line in the green at 65 of the scale, which was double, precisely as the corresponding absorption-line is represented in spectrum No. 2 of the diagram.

Lime.—The experiments were made with the cylinders of lime prepared for use with the oxyhydrogen blowpipe, and also with pieces of pure caustic lime, but there was no sensible difference presented in the spectroscopie.

The bright lines consisted of a double line in the green, and several bands in the orange and red, which were found to form a spectrum identical with that which is produced when chloride of calcium is heated in the flame of a Bunsen's burner.

When the spectroscopie was directed to a point in the flame a little above the incandescent portion of the lime, the lines appeared beyond the bright continuous spectrum, showing that they are not produced by the white-hot solid lime, but by the luminous vapour into which a portion of the lime has been converted by the heat of the flame.

Magnesia.—The commercial heavy oxide of magnesium was made into a paste with distilled water, and formed into a small pellet upon the end of a platinum wire. The pellet of magnesia was slowly dried, and then placed in the oxyhydrogen flame. I was surprised to see a spectrum of bright lines precisely similar to that which is produced by lime. Chloride of magnesium, when introduced into the Bunsen flame, gave a similar spectrum. I record these results as the oxide and chloride were those sold as pure. I found afterwards that a very small trace of lime may be detected in magnesia by means of the oxyhydrogen flame.

I then took metallic magnesium, which I had found by the spectroscopie to be nearly pure, and formed from it magnesia and chloride of magnesium.

When this magnesia, formed into a small ball upon a wire, was sub-

jected to the oxyhydrogen flame, two bright bands were seen in the green. One of these was found to be coincident with the triple line of Fraunhofer's *b*, which distinguishes magnesium, and the other with a group of bright lines which is seen between *b* and F, nearly in the position of the brightest double line of nitrogen, when metallic magnesium is burnt in air.

The chloride formed from magnesium, when introduced into the Bunsen flame, gave the same bands, but the more refrangible band was exceedingly faint.

When an induction-spark was taken from a wire covered with cotton-wool soaked with a solution of the chloride, the lines at *b* and the more refrangible group were seen. If the heating-power of the spark be increased by the introduction of a Leyden jar, the band between *b* and F becomes scarcely distinguishable, while the lines peculiar to metallic magnesium are much more intense. When a spark is taken between electrodes of the same specimen of magnesium from which the chloride was formed, no trace of this band was detected.

Baryta.—When pure caustic baryta is subjected to the heat of the oxyhydrogen flame, a brilliant spectrum is seen identical with the well-known spectrum which presents itself when chloride of barium is heated in the Bunsen flame. Baryta furnishes a larger quantity of vapour than lime and magnesia, and therefore the lines could be traced to a greater distance from the solid baryta.

Strontia.—Pure strontia was fused into a large bead upon a platinum wire. When this bead was heated by the oxyhydrogen flame, the same spectrum of bright lines presented itself as is seen when chloride of strontium is placed in the flame of a Bunsen's burner.

Zirconia.—One of the small pellets of zirconia prepared in France for use with the oxyhydrogen blowpipe was found to give no trace of bright lines. This great fixity of zirconia as compared with lime is in agreement with the inalterability of the substance under the action of the oxyhydrogen flame.

Alumina.—Pure alumina treated in the same way as the magnesia gave a continuous spectrum only, without any trace of bright lines.

Glucina.—Glucina gave a bright line in the red, which I found to be due to potassium. Glucina, therefore, appears not to form vapour of any kind under the heat of the oxyhydrogen blowpipe.

Titanic acid gave a continuous spectrum without lines.

Oxide of uranium a continuous spectrum without lines.

Tungstic acid a continuous spectrum without bright lines.

Molybdic acid a continuous spectrum without bright lines.

Silica (precipitated) a continuous spectrum without bright lines.

Oxide of cerium a continuous spectrum without bright lines.

The question presents itself as to the nature of the vapour to which the bright lines are due in the case of the earths, lime, magnesia, strontia, and baryta. Is it the oxide volatilized? or is it the vapour of the metal reduced by the heat in the presence of the hydrogen of the flame? The experi-

ments show that the luminous vapour is the same as that produced by the exposure of the chlorides of the metals to the heat of the Bunsen gas-flame. The character common to these spectra of bands of some width, in most cases gradually shading off at the sides, is different from that which distinguishes the spectra of these metals when used as electrodes in the metallic state*.

Roscoe and Clifton have investigated the different spectra presented by calcium, strontium, and barium, and they "suggest that at the lower temperature of the flame or weak spark, the spectrum observed is produced by the glowing vapour of some compound, probably the oxide, of the difficultly reducible metal; whereas at the enormously high temperature of the intense electric spark these compounds are split up, and thus the true spectrum of the metal is obtained. In none of the spectra of the more reducible alkaline metals (potassium, sodium, lithium) can any deviation or disappearance of the maxima of light be noticed on change of temperature"†.

As the experiments recorded in this paper show that the same spectra are produced by the exposure of the oxides to the oxyhydrogen flame, Roscoe and Clifton's suggestion that these spectra are due to the volatilization of the compound of the metal with oxygen is doubtless correct.

The similar character of the spectrum of the bright lines seen when erbia is rendered incandescent would seem to suggest whether this earth may not be volatile in a small degree, as is the case with lime, magnesia, and some other earths. The peculiarity, however, of the bright lines of erbia, observed by Bahr and Bunsen, that they could not be seen in the flame beyond the limits of the solid erbia, deserves attention. My own experiments to detect the lines in the Bunsen gas-flame, even when a very thin wire was used, so as to allow the erbia to attain nearly the heat of the flame, were unsuccessful. The bright line in the green appears, indeed, to rise to a very small extent beyond the continuous spectrum, but I was unable to assure myself whether this appearance might not be an effect of irradiation.

It is perhaps worthy of remark that the chlorides of sodium, potassium, lithium, caesium, and rubidium give spectra of defined lines which are not altered in character by the introduction of a Leyden jar, and which, in the case of sodium, potassium, and lithium, we know to resemble the spectra obtained when electrodes of the metals are used. Now all these metals belong to the monad group; it appeared therefore interesting to observe the behaviour of the other metal belonging to this group.

Chloride of silver when introduced into the Bunsen flame gave no lines. The chloride was then mixed with alumina, which had been found to give a continuous spectrum only, and exposed to the oxyhydrogen

* For the spectra of metallic strontium, barium, and calcium, see *Phil. Trans.* 1864, p. 148, and Plates I. and II. Both forms of the spectra of these substances are represented by Thalen in his 'Spektralanalys.'

† Roscoe's *Spectrum Analysis*, p. 175, and *Proc. Lit. & Phil. Soc. Manchester*, April 1, 1862. See also A. Mitscherlich, 'Ueber die Spectren der Verbindungen,' S. 10,

flame, but no lines were visible. When, however, the moistened chloride was placed on cotton and subjected to the induction-spark without a jar, the true metallic spectrum was seen, as when silver electrodes are used.

The behaviour of silver, therefore, is similar to that of the other metals of the monad group. Now the difference in basic relations which is known to exist between the oxides of the monatomic and polyatomic metals would be in accordance with the distinction which the spectroscope shows to exist in the behaviour of the chlorides; the chlorides of the polyatomic metals would be more likely to split up in the presence of water into oxides and hydrochloric acid.

In the case of some of the oxides and chlorides, one or more of the lines appeared to agree with corresponding lines in the metallic spectra; it may be, therefore, that under some circumstances, as in the case of magnesium burning in air, the metallic vapour and the volatilized oxide may be simultaneously present.

Dr. Reynolds's Experiments.

"After you observed the occurrence of two bright lines in the spectrum of the light emitted by incandescent lime, you recollect we identified these as belonging to calcium. At the time we supposed that these lines were produced by the ignition of the vapour of some volatile calcium compound probably present as an impurity in the sample of limes used in the experiments. If this explanation was found to be true for lime, the bright lines seen in the spectrum of erbia might possibly be accounted for in a similar manner. In order to examine the matter fully, I arranged the experiments described below.

"I selected two oxides for comparison with erbia, viz. lime and magnesia. As it seemed desirable to prepare these oxides in precisely the same manner as the erbia, some calcium and magnesium nitrates were made chemically pure to ordinary tests, and then used in the preparation of the respective oxides.

"The oxyhydrogen flame was employed as the chief source of heat. The hydrogen was made from zinc and sulphuric acid in the usual way, and the oxygen from potassium chlorate. As both gases are certain to be contaminated with traces of acids, I took the precaution of passing each gas through a long tube filled with fragments of solid potassium hydrate. If this plan were not adopted, the traces of acid which would find their way into the hydrogen or oxyhydrogen flame might produce volatile compounds with the earths, and so lead to mistakes.

"1. *Experiments with Magnesia.*—A loop of stout platinum wire was moistened with syrupy phosphoric acid, and some magnesium nitrate made to adhere. The nitrate was then heated in the hydrogen flame, and a residue of magnesia obtained. No lines were observed in the spectrum of the light emitted by the incandescent earth, and when the latter was in-

tensely heated in the oxyhydrogen jet only a continuous spectrum was seen*.

“2. *Experiments with Lime.*—A platinum wire of the same thickness as the last was moistened with the phosphoric acid, some calcium nitrate was then taken up in the loop, and heated in the hydrogen flame until a residue of lime was obtained. At the outset the calcium-spectrum was observed, but the light speedily gave only a continuous spectrum. The lime and loop of wire were kept well enveloped in the hydrogen flame for nearly half an hour in order to ensure the complete decomposition of the nitrate. During this time no lines could be detected on the background of the continuous spectrum, or in the spectrum of the flame surrounding the lime. More hydrogen was now turned on and oxygen slowly admitted, the light being examined with the spectroscope during the time. When the proportion of oxygen had reached a certain point, faint traces of the two brightest Ca lines appeared on the bright background, and the intensity of these lines increased with the amount of oxygen admitted up to a definite extent. When a certain proportion of oxygen was exceeded, the lines became less distinct. The best results were obtained when the hydrogen was decidedly in excess of the oxygen in the flame, that is to say, more than in the proportion of 2 : 1.

“When the slit of the spectroscope was pointed in such a way that only the light from the flame surrounding the incandescent lime entered the instrument, all the Ca lines and bands were observed with great ease without a continuous spectrum. On looking at the mantle of flame with the naked eye it was easy to perceive a reddish tinge. I next maintained the small fragment of lime at the highest temperature its supporting wire was capable of resisting for *three hours*; at the end of this time the Ca lines were as strongly marked as before, and the lime on the wire had very appreciably diminished in amount. The same results were obtained when no phosphoric acid was employed to attach the calcium nitrate to the wire in the first instance.

“Again, a piece of well-burned quicklime, of very small size, was heated alone on a platinum wire for more than an hour, and the bright Ca lines were seen during the whole time.

“From the results of these experiments, we must draw the conclusions (1) that when lime is sufficiently heated the light which it emits is derived in part from the incandescent solid, and partly from ignited vapour; (2) that lime is either volatile *as such*, or that in the first instance it suffers reduction by the excess of hydrogen in the flame, the luminous vapour of calcium then giving its own peculiar spectrum.

“3. *Experiments with Erbium.*—The specimen of erbium nitrate which

* “Since writing the above, I have succeeded in observing the bright lines described by Mr. Huggins as occurring in the spectrum of the flame surrounding the incandescent magnesia. In the earlier experiments I probably admitted too much oxygen to the mixed gas-flame in the first instance.”

you kindly gave me was attached to a platinum loop with syrupy phosphoric acid as usual, and decomposition of the salt effected in the plain hydrogen flame. After heating for a short time in this way, the chief green line of erbium became visible, but seen upon the continuous spectrum. Oxygen was now turned slowly into the flame. As the temperature rose, two of the other bright lines of the earth were seen. The best observations were made when the oxyhydrogen flame had hydrogen in excess, and the erbium was kept in such a position that it was very strongly ignited. The erbium lines were most distinctly seen when the slit of the spectroscope took in the light from the extreme edge of the incandescent solid. When the bright lines were best observed, the continuous spectrum was relatively faint. Again, when the slit was made to cut the edge of the ignited bead of the earth, the strong green line of erbium was seen to extend to a very small but appreciable distance above or below (as the case might be) the continuous spectrum. I could only observe this for the strong line. I failed to get any trace of lines in the spectrum of the flame beyond the incandescent erbium.

"The erbium was next heated in the oxyhydrogen flame to the maximum temperature that the wire would bear for *three and a half hours*, but the green line was seen to be just as strongly marked at the end as at the beginning of the experiment. The bulk of the erbium was so much reduced by this treatment, that I have now scarcely a trace left.

"From the results of these experiments, I think we must conclude (1) that the light emitted by incandescent erbium is derived chiefly from the ignited solid, but that the bright lines observed in its spectrum have as their source a luminous vapour of extremely low tension at even the highest temperature of the oxyhydrogen flame; (2) that this interrupted spectrum belongs either to erbium or to its oxide.

"If these conclusions are true, it follows that erbium is not an exception to the ordinary law.

"It would appear that in these experiments three substances have been employed, varying in their degree of volatility. At the temperature of the oxyhydrogen flame magnesia appears to be less volatile than lime; but I am in doubt what relative volatility to assign to erbium, since its spectrum of bright lines can be seen when the earth is heated in the plain hydrogen flame, and yet at the much higher temperature of the oxyhydrogen jet the volume of luminous vapour does not appear to materially increase.

"Finally, we have yet to learn whether or not in all these cases reduction of the oxide precedes volatilization; if reduction takes place, the luminous vapour must be that of the metal. The settlement of this question would no doubt be very difficult. But I rather incline to the view that the vapour whose spectrum is obtained on igniting these earths is that of the metal; for I find that the bright lines are most easily observed when hydrogen is present in excess in the oxyhydrogen flame. Moreover, the actual amount of matter volatilized on very prolonged heating is really very

small, and this circumstance appears to favour the view that a slow surface-reduction is in progress."

XII. "On the Values of the Integrals $\int_0^1 Q_n, Q_{n'}, d\mu, Q_n, Q_{n'}$ being Laplace's Coefficients of the Orders n, n' , with an application to the Theory of Radiation." By the Hon J. W. STRUTT, Fellow of Trinity College, Cambridge. Communicated by W. SPOTTISWOODE, F.R.S. Received May 17, 1870.

(Abstract.)

These integrals present themselves in calculations dealing with arbitrary functions on the surface of a sphere which vary discontinuously in passing from one hemisphere to the other. When n, n' are both even or both odd, the values of the integrals may be immediately inferred from known theorems in which the integration extends from -1 to $+1$, or over the whole sphere; otherwise a special method is necessary. In the present paper a function of two variables is investigated, which, when expanded, has for coefficients the quantities in question. As an example of the method, the problem is taken of a uniform conducting sphere exposed to the heat proceeding from a radiant point. It will appear at once that the heat received by any element of the surface is expressed by different analytical functions on the two hemispheres—a source of discontinuity which renders necessary a special treatment of the problem. The solution is afterwards generalized to meet the case of a sphere exposed to any kind of radiation from a distance.

One remarkable result not confined to the sphere is, that the effect of a radiation which is expressed by one or more harmonic terms of odd order is altogether nil, with the single exception of the term of the first order.

XIII. "Note on the Construction of Thermopiles." By the EARL OF ROSSE, F.R.S. Received June 14, 1870.

Although in the measurement of small quantities of radiant heat by means of the thermopile much may be done towards increasing the sensibility of the apparatus by carefully adjusting the galvanometer and rendering the needle as nearly astatic as possible, there must necessarily be some limit to this, and it therefore appears desirable that the principles on which thermopiles of great sensibility can be constructed should also be carefully attended to.

With the view of obtaining a pair of thermopiles of greater sensibility and of more equal power than I had been able to procure ready made, I made a few experiments with various forms of that instrument, and I was led to the conclusion (one which might have been foreseen) that the

